CANMET

REPORT 83-4E

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

AN EVALUATION OF TWO METHODS FOR THE DETERMINATION OF INDIUM IN ORES, CONCENTRATES AND ZINC PROCESSING PRODUCTS BY FLAME ATOMIC-EMISSION AND FLAME ATOMIC-ABSORPTION SPECTROPHOTOMETRY

ELSIE M. DONALDSON

MICROMEDIA
AUG 29 1983

34 pp

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES

MARCH 1983

Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

Canada

© Minister of Supply and Services Canada 1983

Available in Canada through

Authorized Bookstore Agents
and other bookstores

or by mail from

Canadian Government Publishing Centre
Supply and Services Canada
Hull, Quebec, Canada K1A 0S9

CANMET
Energy, Mines and Resources Canada,
555 Booth St.,
Ottawa, Canada K1A 0G1

or through your bookseller

Catalogue No. M38-13/83-4E
ISBN 0-660-11394-5

Canada: $3.00
Other countries: $3.60

Price subject to change without notice.

© Ministre des Approvisionnements et Services Canada 1983

En vente au Canada par l'entremise de nos

agents libraires agréés
et autres librairies

ou par la poste au:

Centre d'édition du gouvernement du Canada
Approvisionnements et Services Canada
Hull, Québec, Canada K1A 0S9

CANMET
Énergie, Mines et Ressources Canada,
555, rue Booth
Ottawa, Canada K1A 0G1

ou chez votre libraire.

Nº de catalogue M38-13/83-4E
ISBN 0-660-11394-5

Canada: $3.00
Hors Canada: $3.60

Prix sujet à changement sans avis préalable.

AN EVALUATION OF TWO METHODS FOR THE DETERMINATION OF INDIUM IN ORES, CONCENTRATES AND ZINC PROCESSING PRODUCTS BY FLAME ATOMIC-EMISSION AND FLAME ATOMIC-ABSORPTION SPECTROPHOTOMETRY

by

Elsie M. Donaldson*

ABSTRACT

Two methods for the determination of small amounts of indium in ores, concentrates and zinc processing products have been evaluated. A method involving the separation of indium from matrix elements by n-butyl acetate extraction as the bromide yields more accurate and precise results than a method based on the coprecipitation of indium with hydrous ferric oxide. For small amounts of indium, a flame atomic-emission finish gives greater accuracy and precision than an atomic-absorption finish. The enhancing effects of aluminum on the determination of indium by both flame atomic-emission and atomic-absorption spectrophotometry in nitric and hydrochloric acid media have been studied and a possible mechanism is proposed to explain the anomalous behaviour observed in the absence and presence of potassium as an ionization suppressant.

*Research Scientist, Research - Special Projects, Mineral Sciences Laboratories, Energy, Mines and Resources, Canada, Ottawa.

Errata Sheet for CANMET Report 83-4E

AN EVALUATION OF TWO METHODS FOR THE DETERMINATION OF INDIUM IN ORES, CONCENTRATES AND ZINC PROCESSING PRODUCTS BY FLAME ATOMIC-EMISSION AND FLAME ATOMIC-ABSORPTION SPECTROPHOTOMETRY by Elsie M. Donaldson

Page 12, Table 3: table heading should read "Sample" and not "Sample and mass taken".

UNE ÉVALUATION DE DEUX MÉTHODES POUR DÉTERMINER LA TENEUR EN INDIUM DANS LES MINERAIS, LES CONCENTRÉS ET LES PRODUITS DE TRAITEMENT DU ZINC, SOIT LA SPECTROPHOTMÉTRIE À ÉMISSION ATOMIQUE ET À ABSORPTION ATOMIQUE À FLAMME

par

Elsie M. Donaldson*

RÉSUMÉ

On a évalué deux méthodes pour la détermination de faibles quantités d'indium dans les minerais, les concentrés et les produits de traitement du zinc. La méthode impliquant la séparation de l'indium des éléments de la matrice par extraction à l'acétate n-butyl sous forme de bromure, a donné des résultats plus précis et plus exacts que la méthode basée sur la co-précipitation de l'indium avec l'oxyde ferrique hydraté. Pour les petites quantités d'indium, une analyse completée par émission atomique à flamme donne plus de précision et d'exactitude que celle par absorption atomique. Les effets positifs de l'aluminium pour la détermination de l'indium par spectrophotométrie à émission atomique et à absorption atomique à flamme en milieu acide (acides nitrique et hydrochlorique) ont été étudiés et on propose un mécanisme possible pour expliquer le comportement anormal observé en l'absence ou en la présence de potassium pour supprimer l'ionisation.

---

*Chercheur scientifique, Recherche - Projets spéciaux, Laboratoires des sciences minérales, Energie, Mines et Ressources Canada, Ottawa.

CONTENTS

	Page
ABSTRACT	i
RÉSUMÉ	ii
INTRODUCTION	1
EXPERIMENTAL	1
Apparatus	1
Reagents	2
Choice of Reference and Other Materials	2
Procedure Used for Sample Decomposition	3
Iron Collection Method	3
Calibration solutions	3
Procedure	3
Extraction Method	4
Calibration solutions	4
Procedure	4
RESULTS AND DISCUSSION	5
Development of the Iron Collection - FAES Method	5
Study of the Interference of Aluminum on the Determination of Indium by FAES AND AAS	6
Elimination of Interference from Aluminum in the Determination of Indium by FAES	9
Effect of Other Elements on the Determination of Indium by FAES After Separation by Iron Collection	10
Application of the Iron Collection and Extraction Methods to CCRMP Reference Materials and Zinc Processing Products	10
Comparison of FAES and AAS Results for Indium	13
CONCLUSIONS	13
REFERENCES	15

TABLES

No.		
1.	Instrumental settings	2
2.	Effect of diverse ions on the FAES determination of indium in nitric acid media	11
3.	Results obtained by FAES for CCRMP ores and concentrates and for zinc processing products by the iron collection and extraction methods	12
4.	Results obtained by FAES for CCRMP ores and concentrates by the iron collection and extraction methods after addition of indium	12
5.	Comparison of FAES and AAS results for indium	13
6.	Precision for indium by FAES and AAS after separation by extraction	14

CONTENTS (cont'd)

Page

FIGURES

1. Effects of potassium, iron (III) and aluminum on the determination of indium by FAES 5
2. Effect of aluminum on the determination of indium by FAES in nitric acid media 6
3. Effect of aluminum on the determination of indium by AAS in nitric acid media 7
4. Effect of aluminum on the determination of indium by FAES in hydrochloric acid media 8
5. Effect of aluminum on the determination of indium by AAS in hydrochloric acid media 9

INTRODUCTION

A current long-term CANMET project involves a study of the behaviour, form and distribution of silver in conventional hydrometallurgical processes designed to recover metallic zinc from zinc ores and concentrates. The objective of this project is to increase the recovery of silver in Canadian zinc plants. Because indium, which is also a valuable by-product, affects the behaviour of silver in the zinc circuit, a reliable and reasonably simple and rapid method was required for the determination of small and moderate amounts of indium in zinc ores, concentrates and processing products.

In recent years, the method used most often at CANMET for the determination of indium in Canadian Certified Reference Materials Project (CCRMP) candidate reference materials involves an atomic-absorption spectrophotometric (AAS) finish after separation of indium from the matrix elements by n-butyl acetate extraction of indium bromide from a 5 M hydrobromic acid medium. Indium is subsequently stripped into water and preconcentrated by evaporation before the determinative step (1). Similar methods, with either AAS or flame atomic-emission spectrophotometric (FAES) finishes applied directly to the extract or, ultimately, to an aqueous solution of indium, have been reported in the literature (2-8). Recently, extraction-AAS methods based on chelation [cinnamoyl-phenylhydroxylamine (9), potassium xanthate (10), sodium diethyldithiocarbamate and other dithiocarbamates (11), bis (2-ethylhexyl) hydrogen phosphate and bis (2-ethylhexyl) hydrogen dithiophosphate (12)] and ion-association iodide-amine extraction systems (13) have also been applied to ores and other materials. However, because of their lack of selectivity, none of these methods were considered to be more advantageous for the determination of indium in the materials under consideration than the bromide-extraction method. Several investigators have reported AAS or FAES methods involving the preliminary separation of indium from zinc, copper and other matrix elements by coprecipitation with hydrous ferric oxide from an ammoniacal medium, followed by the separation of indium from iron and other coprecipitated elements by extraction as the iodide or bromide (6-8). In these methods, indium is ultimately determined by spraying either the extract, or the aqueous solution obtained after a suitable stripping step, into the flame. However, an iron collection step alone, in conjunction with a FAES finish, has been applied to iron slimes and cakes (14). Because it was considered that a method involving the coprecipitation of indium with iron (III) would probably be more rapid than the bromide-extraction method used at CANMET (1) and might be advantageous in routine work where a large number of samples are to be analyzed, the applicability of this method was investigated in the present work. The bromide-extraction method was also evaluated because the final preconcentration step makes it applicable to samples containing microgram-quantities of indium. In this work, more emphasis was placed on a FAES finish than an AAS finish because, in a nitrous oxide-acetylene flame, FAES is about 25 times more sensitive than AAS in an air-acetylene flame (15). During the investigation of the extraction method, no attempt was made to determine indium by direct atomization of the n-butyl acetate extract because aqueous calibration solutions are usually more stable, much easier to prepare and considerably more convenient to use particularly for routine work. Some results obtained by FAES are compared with those obtained by AAS.

EXPERIMENTAL

APPARATUS

A Varian-Techtron Model AA6 spectrophotometer, equipped with a chopper, a 6-cm laminar-flow nitrous oxide-acetylene burner, a 10-cm laminar-flow air-acetylene burner and an indium hollow-cathode lamp, was used under the conditions given in Table 1. For flame atomic-emission measurements, calibration ranges of 0-2 or 0-3 µg of indium per mL for 0 to 100% emission were set with distilled water and the appropriate calibration solution.

Table 1 - Instrumental settings

Parameters	FAES		AAS	
	N_2O-C_2H_2	Air-C_2H_2	N_2O-C_2H_2	Air-C_2H_2
Wavelength (nm)	451.1	451.1	303.9	303.9
Lamp current (mA)	-	-	5	5
Spectral band-pass (nm)	0.1	0.1	0.2	0.2
Height of burner (mm)	15	10	6	4
Acetylene flowmeter reading	6.5 (~4.5 L/min)	2.5 (1.7 L/min)	6.5 (~4.5 L/min)	2.0 (1.5 L/min)
Nitrous oxide flowmeter reading	6.25 (~8.5 L/min)	-	6.25 (~8.5 L/min)	-
Air flowmeter reading	-	6.5 (11.5 L/min)	-	6.5 (11.5 L/min)
Flame	0.5 cm red feather	Oxidizing	Oxidizing	Oxidizing
Aspiration rate (mL/min)	8	8	8	8

REAGENTS

Standard indium solution, 1000 µg/mL. Pure indium metal (0.5000 g) was dissolved by warming gently with 20 mL of 50% nitric acid and the resulting solution was diluted to 500 mL with water. A 100-µg/mL solution containing ~0.5% by volume of nitric acid was prepared by diluting 20 mL of the stock solution and 1 mL of concentrated nitric acid to 200 mL with water. A 10-µg/mL solution was prepared by diluting 10 mL of the 100-µg/mL solution to 100 mL with water.

Aluminum (10 000 µg/mL) - potassium (20 000 µg/mL) solution. Aluminum monohydrate [140 g of $Al(NO_3)_3 \cdot 9H_2O$] and 51.7 g of potassium nitrate were dissolved in about 800 mL of water and the solution was diluted to 1 L.

Iron (III) nitrate solution, 10 mg iron/mL. Ferric nitrate monohydrate [72.3 g of $Fe(NO_3)_3 \cdot 9H_2O$] was dissolved in ~300 mL of hot water containing 5 mL of concentrated nitric acid and the solution was cooled and diluted to 1 L with water.

Bromine-carbon tetrachloride solution, 20% V/V. Approximately 20 mL of bromine was mixed with 80 mL of carbon tetrachloride in a glass-stoppered bottle.

Hydrobromic acid, 5 M. Approximately 570 mL of concentrated (8.8 M) hydrobromic acid was diluted to 1 L with water.

Potassium solution, 20 000 µg/mL. Potassium nitrate (51.7 g) was dissolved in water and the solution was diluted to 1 L.

Nitric acid, 1%, 20% and 50% V/V.

Sulphuric acid, 50% V/V.

Ammonium hydroxide, 5% V/V.

N-Butyl acetate, equilibrated. Aproximately 200 mL of reagent-grade solvent was shaken for about 1 min with an equal volume of 5 M hydrobromic acid.

CHOICE OF REFERENCE AND OTHER MATERIALS

Four Canadian Certified Reference Materials Project (CCRMP) ores and concentrates were chosen for use in this work because of their accurately known indium contents. Four other CCRMP reference materials - to which known amounts of indium were added - and various zinc processing products (previously reground and mixed thoroughly) were also employed.

PROCEDURE USED FOR SAMPLE DECOMPOSITION

Depending on the indium content, from 0.2-1 g of powdered sample was treated, in a covered 400-mL teflon beaker*, with 20 mL of 50% nitric acid and 5 mL of 20% bromine-carbon tetrachloride solution to oxidize sulphur and sulphides to sulphate. The mixture was allowed to stand for about 15 min, then the solution was heated gently to remove bromine and carbon tetrachloride, 20 mL of 50% sulphuric acid and 5 mL of concentrated hydrochloric acid were added and the solution was heated to remove oxides of nitrogen. After removing the cover, the sides of the beaker were washed down with water, 5 mL of concentrated hydrofluoric acid was added and the solution was evaporated to fumes of sulphur trioxide. The solution was cooled, 20 mL of water and 10 mL of concentrated hydrobromic acid were added and the solution was heated to dissolve the salts. The resulting solution was transferred to a 400-mL pyrex beaker, then, depending on the method used, it was either evaporated to dryness or until ~5 mL of sulphuric acid remained - to ensure the removal of hydrofluoric acid and to volatilize arsenic, antimony, tin and selenium as the bromides.

IRON COLLECTION METHOD

Calibration Solutions

Calibration solutions containing 0.2, 0.4, 0.6, 1, 1.5, 2, 2.5 and 3 µg of indium per mL were prepared by adding the required volumes of the 10- or 100-µg/mL indium solution to 100-mL volumetric flasks containing 15 mL of 10 mg/mL iron (III) solution (as nitrate), 10 mL of 10 000-µg/mL aluminum - 20 000-µg/mL potassium solution and 5 mL of concentrated nitric acid. The resulting solutions were diluted to volume with water. A zero calibration solution was prepared in a similar manner. These solutions were stable for at least one month.

*For samples containing about 1% or less of silica, a pyrex beaker was used and the addition of hydrofluoric acid was omitted.

Procedure

After sample decomposition as described above and evaporation of the solution to ~5 mL, ~100 mL of water and 5 mL of concentrated hydrochloric acid were added to the solution, then, if necessary, sufficient 10 mg/mL iron (III) solution was added so that ~150 mg of iron was present. The resulting solution was heated to dissolve the soluble salts, then cooled to room temperature and sufficient concentrated ammonium hydroxide was added to precipitate iron as the hydrous oxide. Approximately 5 mL of ammonium hydroxide was added in excess, the beaker was covered and the solution was boiled for ~1 min to coagulate the precipitate. The precipitate was allowed to settle, then the solution was filtered, using Whatman No. 541 paper, and the beaker was washed twice with 5% ammonium hydroxide. The paper and precipitate were washed twice with 5% ammonium hydroxide, then once with water and the bulk of the precipitate was washed back into the original beaker with water. After the addition of 5 mL of concentrated nitric acid, the solution was heated to dissolve the precipitate and, if necessary, evaporated to ~50 mL. The resulting solution was filtered, through the same filter paper, into a 100-mL volumetric flask containing 10 mL of 10 000 µg/mL aluminum - 20 000 µg/mL potassium solution and the beaker was washed twice with 5-10-mL portions of hot 1% nitric acid, then once with ~5 mL of water. The paper was washed in a similar manner, then discarded and the solution was diluted to volume with water*.

For FAES measurements, the spectrophotometer was adjusted to the appropriate calibration range and the emission of the resulting solution was measured at 451.1 nm in a 0.5 cm "red feather" nitrous oxide-acetylene flame. The indium content of the solution (in µg) was calculated from the emission values obtained for the solution and those obtained concurrently for calibration solu-

*Solutions that were cloudy or contained insoluble material, e.g., lead sulphate or manganese dioxide, were filtered through a dry Whatman No. 42 paper before making emission or absorption measurements.

tions that bracketed the sample concentration. Five or six measurements were taken for each sample solution and the mean concentration of indium found was used to calculate the indium content of the sample.

For AAS measurements, the absorption of the solution was measured at 303.9 nm in an oxidizing air-acetylene flame using tenfold scale expansion and the indium content of the sample was ultimately calculated as described above using the mean concentration value found from five or six measurements.

EXTRACTION METHOD

Calibration Solutions

Calibration solutions containing 0.2, 0.4, 0.6, 1, 1.5, 2, 2.5 and 3 μg of indium per mL were prepared by adding the required volumes of the 10- or 100-μg/mL indium solution to 100-mL volumetric flasks containing 10 mL of 20 000-μg/mL potassium solution and 2 mL of concentrated nitric acid. The resulting solutions were diluted to volume with water. A zero calibration solution was prepared in a similar manner. These solutions were stable for at least one month.

Procedure

After sample decomposition as described above and evaporation of the solution to dryness, 30 mL of concentrated hydrobromic acid was added to the beaker and the solution was heated gently to dissolve the salts. After cooling the solution, 3 g of ascorbic acid was added to reduce iron (III), the beaker was swirled to dissolve the reductant, then, using 11-cm Whatman No. 40 paper, the solution was filtered into a 125-mL separatory funnel marked at approximately 50 mL. The beaker was washed three times with 3- or 4-mL portions of water, then the paper was washed twice with ~4-mL portions and discarded. If necessary, the resulting solution was diluted to 50 mL with water, mixed thoroughly to reduce the iron present, then 50 mL of equilibrated n-butyl acetate was added and the funnel was closed tightly and shaken for 2 min. After the layers separated, the lower aqueous layer was drained into a second 125-mL separatory funnel. To remove the aqueous layer remaining in the bore of the stop-cock of the first funnel, from 1-2 mL of 5 M hydrobromic acid, contained in a plastic squeeze-type wash bottle, was added to the first funnel containing the extract, then, without mixing, the resulting aqueous layer was drained into the second funnel. The stem of the first funnel was washed with 5 M hydrobromic acid, the washings were collected in the second funnel and the solution was re-extracted by shaking it for 1 min with 25 mL of equilibrated n-butyl acetate. After draining off and discarding the aqueous layer, the stem of the second funnel was washed with water, the second extract was added to the first extract and the second funnel was washed with non-equilibrated n-butyl acetate contained in a plastic squeeze-type wash-bottle. The combined extract was washed once by shaking it for ~30 s with 5 mL of 5 M hydrobromic acid and the wash solution was drained off and discarded. Indium was subsequently stripped from the organic phase by shaking it for 1 min with 20 mL of water, then for 30 s each time with a 20- and 10-mL portion of water. The aqueous layers were collected in a 150-mL beaker and the stem of the funnel was washed with water each time*. The resulting solution was evaporated to ~10 mL, then 4 mL of 50% nitric acid was added and the solution was covered and heated to remove bromine and oxides of nitrogen. After removing the cover, the solution was evaporated to dryness, then, depending on the indium content, sufficient 20% nitric acid and 20 000-μg/mL potassium solution were added so that 1 mL of each would be present for each 10 mL of final solution. The solution was heated gently for 1 or 2 min to dissolve the salts, then cooled to room temperature, transferred to a volumetric flask of appropriate size (10-200-mL) and diluted to volume with water. The indium content of the resulting solution was determined by FAES or AAS as described above.

*The n-butyl acetate was used for subsequent extractions after the combined organic phase, contained in a large separatory funnel, was washed once with water followed by re-equilibration with 5 M hydrobromic acid.

RESULTS AND DISCUSSION

DEVELOPMENT OF THE IRON COLLECTION - FAES METHOD

Experimental details of the iron collection method previously reported for the determination of small amounts of indium in iron slimes and cakes by FAES were not available because it appears in an obscure Soviet journal (14). Furthermore, no information on the procedure is given in the abstract. Consequently, some preliminary work was necessary to determine the optimum conditions required for the coprecipitation step and for the ultimate determination of indium by FAES. Investigations showed that, in the presence of ~150 mg of iron (III), up to at least 250 µg of indium can be quantitatively separated by coprecipitation with hydrous ferric oxide from an ammoniacal medium containing ~5% by volume of ammonium hydroxide in excess. This amount of iron (III) was chosen to allow the use of a mass of up to 1 g for samples containing up to ~15% of iron. The presence of more than ~150 mg of iron (III) during the coprecipitation step is not practicable because of the bulk of the precipitate. Because ultimately it was also desired to compare results obtained by both FAES and AAS, nitric acid was chosen for the dissolution of the precipitate because it interferes less than hydrochloric and other acids in the AAS determination of indium (16-19). Hydrochloric acid suppresses indium absorption because of the formation of diatomic indium chloride (InCl) molecules in the flame. The dissociation energy of this molecule is large enough so that it is not readily dissociated into atoms even in a nitrous oxide-acetylene flame (18,19). Hydrochloric acid has also been reported to depress indium emission in high-temperature flames (20). Figure 1 shows that the addition of ~2000 µg of potassium (as nitrate) per mL to dilute nitric acid solutions of indium, as recommended in both FAES and AAS to suppress the ionization of indium (15,21), causes a significant increase in the sensitivity by FAES (cf. curve b) - i.e., ~17% at the 2-µg/mL level after correction for the resultant increase in background. Figure 1 also shows that the presence of ~1500 µg of iron (III) per mL (curve c) causes only a slight further enhancing effect. In subsequent work, this error from iron was minimized by adding 150 mg of iron (III) (as nitrate) to the calibration solutions and sufficient iron (III), if necessary, to the sample solutions so that ~150 mg would be present during the coprecipitation step. Although the curves shown in Fig. 1 are not linear, the positive error produced is essentially negligible when indium contents are calculated by relating the emission value obtained for the sample solution to those obtained concurrently for calibration solutions that closely bracket the sample concentration.

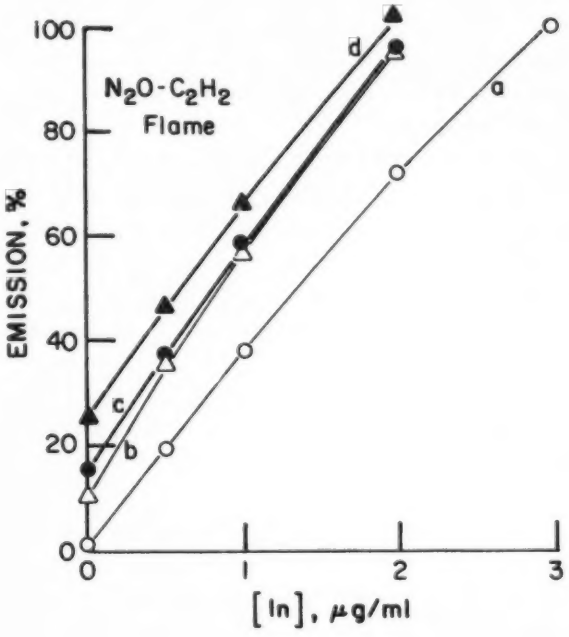

Fig. 1 - Effects of potassium, iron (III) and aluminum on the determination of indium by FAES

a - 5% HNO_3
b - 5% HNO_3 + 2000 µg K/mL
c - 5%HNO_3 + 2000 µg K/mL + 1500 µg Fe(III)/mL
d - 5%HNO_3 + 2000 µg K/mL + 1500 µg Fe(III)/mL + 1000 µg Al/mL

Zero % emission set with distilled water; 100% emission set with a 3 µg/mL In solution containing 5% by volume of nitric acid

STUDY OF THE INTERFERENCE OF ALUMINUM ON THE DETERMINATION OF INDIUM BY FAES AND AAS

Tests carried out to study the effects of various elements that would be coprecipitated or largely occluded by the hydrous ferric oxide precipitate showed that, in a dilute nitric acid medium, aluminum, which is usually present in ores, strongly enhances indium emission in a nitrous oxide-acetylene flame (cf. curve d, Fig. 1). Figure 2 shows that, in both nitrous oxide-acetylene and air-acetylene flames, the enhancing effect of aluminum is considerably greater in the absence of potassium than in its presence. Although Fig. 2 (curve c) shows that, at the 10-µg/mL indium level, 3000 µg of aluminum per mL slightly suppresses indium emission in an air-acetylene flame in the presence of 2000 µg of potassium per mL, probably this is largely the result of instrumental error because, for the five or six measurements taken in these tests and in all subsequent work, the standard deviation of the FAES determination at this level was found to be about ±0.10 µg/mL. Some further tests carried out to help elucidate the anomalous behaviour of aluminum [Fig. 3(a) and (b)] showed that the same effect, although of lesser magnitude, also occurs when indium is determined by AAS in nitrous oxide-acetylene and air-acetylene flames. Some previous investigators have reported that aluminum suppresses indium emission in nitrous oxide-acetylene (15) and oxy-hydrogen flames (22), suppresses indium absorption in air-acetylene flames (9,23) and enhances it in nitrous oxide-acetylene flames (16). The large enhancement in the results obtained for indium emission (Fig. 2, curve b) and absorption [Fig. 3(b), curve f] in the nitrous oxide-acetylene flame in the absence of potassium strongly suggests that, in the presence of nitric acid, in which the species In-O and $In-NO_3$ are in equilibrium ($In-O-NO_3$), aluminum is acting as a releasing agent. According to the following equation:

$$In-O-NO_3 + Al^{+3} \underset{\text{excess } Al^{+3}}{\rightleftharpoons} Al-O-NO_3 + In$$

the reaction proceeds to the right when aluminum is present in excess. This results in the production of a greater proportion of free indium atoms which would explain the observed increases in emission and absorbance (24). The plateau in Fig. 2 (curve a) in the presence of potassium and the subsequent increase in the apparent indium content of the test solutions with increasing aluminum concentration suggests the formation in the flame of a stable potassium-aluminum species such as potassium aluminate, $KAlO_2$. To form this compound, the amount of potassium (200 mg) present in

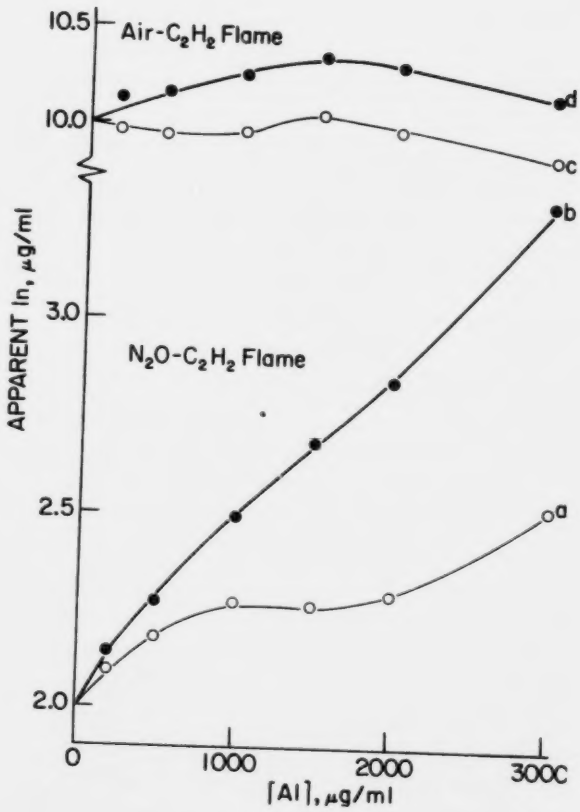

Fig. 2 - Effect of aluminum on the determination of indium by FAES in nitric acid media

a and c - 2000 µg K/mL present in the test and calibration solutions

b and d - K absent in the test and calibration solutions

All solutions contained 5% by volume of nitric acid

the test solutions must react with 138 mg of aluminum, which corresponds to a concentration of 1380 µg/mL in the final solution. Consequently, as shown in curve a, the interference from aluminum should increase at concentrations greater than ~1400 µg/mL. In the AAS tests, the formation of potassium aluminate is also indicated [Fig. 3(b), curve e] by the elimination of the interference from aluminum in the nitrous oxide-acetylene flame when the test solutions contained 2000 µg of potassium per mL. The decrease in the emission (Fig. 2) and absorption [Fig. 3(a) and (b)] in the presence of potassium may be caused by a recombination reaction between indium and oxygen formed by thermal decomposition of potassium nitrate in the flame (25). The differences in the magnitudes of the effects of aluminum in the presence and absence of potassium in the FAES and AAS determinations of indium in the air-acetylene and nitrous oxide-acetylene flames are largely caused by the difference in flame temperature. In atomic-absorption spectrophotometry, interference effects are usually less in the hotter nitrous oxide-acetylene flame than in an air-acetylene flame [cf., curve e, Fig. 3(b) with curves a and c, Fig. 3(a)] because interelement compounds are more readily dissociated in the hotter flame. However, the greater enhancing effect of aluminum on the

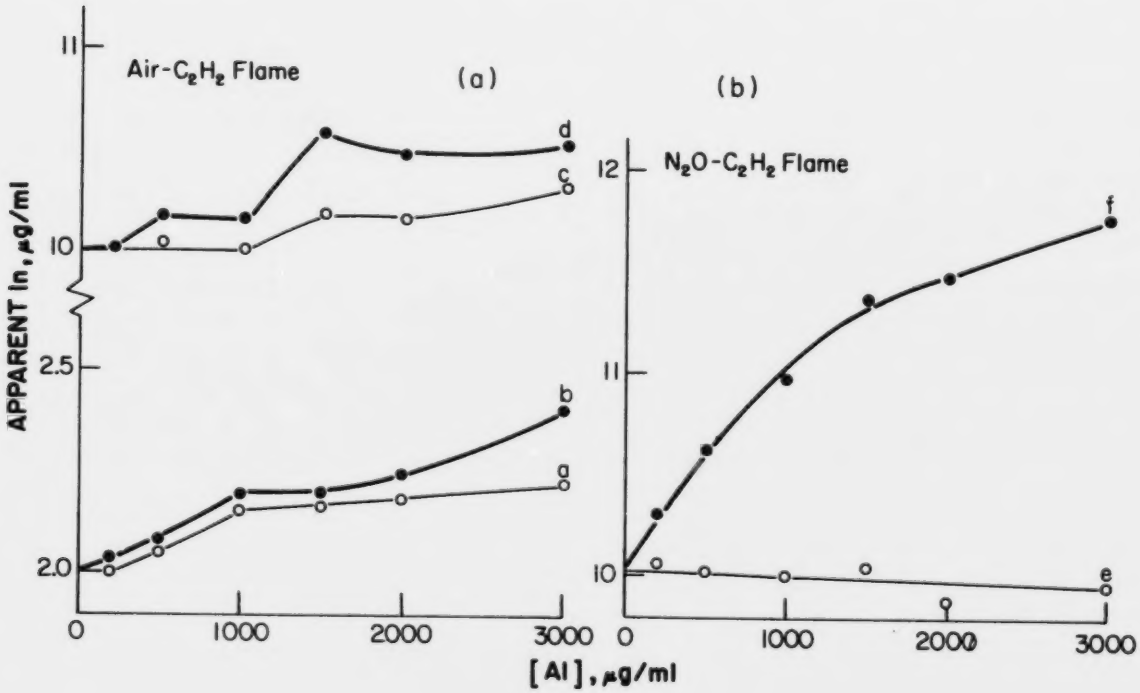

Fig. 3(a) and (b) - Effect of aluminum on the determination of indium by AAS in nitric acid media

a, c and e - 2000 µg K/mL present in the test and calibration solutions

b, d and f - K absent in the test and calibration solutions

All solutions contained 5% by volume of nitric acid. Five-fold scale expansion used at the 10-µg/mL In level; ten-fold used at the 2-µg/mL level

determination of indium by AAS in the nitrous oxide-acetylene flame [curve f, Fig. 3(b)] in the absence of potassium compared with the air-acetylene flame [curve d, Fig. 3(a)] is probably caused by the greater ease with which Al-O compounds are dissociated in the hotter flame (21). This would result in the production of more free aluminum atoms and, subsequently, in the formation of more free indium atoms. In flame-emission spectrophotometry, interference effects are usually greater in the hotter flames because of increased excitation of, and interactions between, atoms (24).

In a very recent paper, Bernal et al. (26) reported that aluminum weakly suppresses indium absorption in hydrochloric acid media in air-acetylene and nitrous oxide-acetylene flames and strongly enhances indium emission in both flames. To determine whether the use of a hydrochloric acid medium might by advantageous, particularly for an AAS finish, after the separation of indium by collection with iron (III), the effect of aluminum (as chloride) was investigated in hydrochloric acid media under the same conditions used to study its effect in nitric acid media. Figures 4 and 5 show that, except for AAS in an air-acetylene flame (Fig. 5, curve c), the results obtained in the presence of aluminum and in the absence and presence of potassium are similar to those obtained for nitric acid media. The plateau in Fig. 5 (curve a) again suggests the formation of potassium aluminate. Although curve c shows that, at the 10-µg/mL indium level, the presence of both aluminum and potassium results in the suppression of indium absorption, some additional tests showed that, at the 2-µg/mL level, ~11% and 6% enhancement was obtained in the absence and presence of 2000 µg of potassium per mL, respectively, for solutions containing 3000 µg of aluminum per mL. The reason for this is not immediately apparent, but it could explain the conflicting results reported by previous investigators who carried out studies at varying levels of indium in different acid media (9,15,16,22,23).

Figures 2-5 show that, for both FAES and AAS, potassium is more effective in eliminating or minimizing interference from aluminum in nitric acid media than in hydrochloric acid media. This is most readily apparent for nitrous oxide-acetylene flames by comparing curve a, Fig. 2, with curve a, Fig. 4 and curve e, Fig. 3(b), with curve a, Fig. 5. The most probable reason for this is that the greater proportion of oxygen molecules in the flame in nitric acid media compared with hydrochloric acid media results in the formation of a larger amount of the potassium aluminate spe-

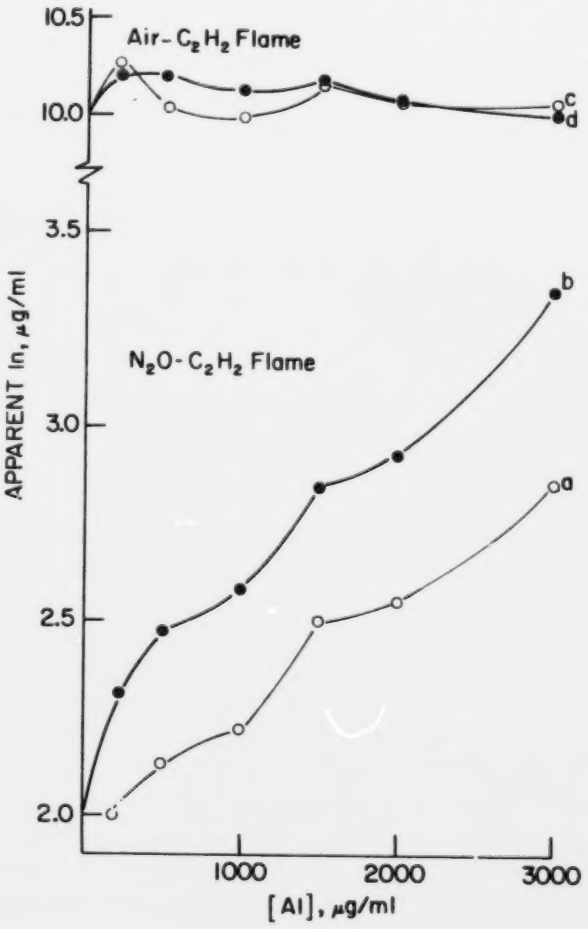

Fig. 4 - Effect of aluminum on the determination of indium by FAES in hydrochloric acid media

a and c - 2000 µg K/mL present in the test and calibration solutions

b and d - K absent in the test and calibration solutions

All solutions contained 10% by volume of hydrochloric acid

cies in the flame. Consequently, the enhancing effect of aluminum is decreased to a greater extent in nitric acid media than in hydrochloric acid media. Some of the curves shown in Fig. 2-5 [i.e., particularly c and d in Fig. 2 and 4, curve e in Fig. 3(b) and curve d in Fig. 5] are not strictly reproducible because of the instrumental errors involved in the FAES and AAS determinations at the 10-µg/mL indium level - i.e., standard deviations of ~±0.1 and ±0.2 µg/mL, respectively for

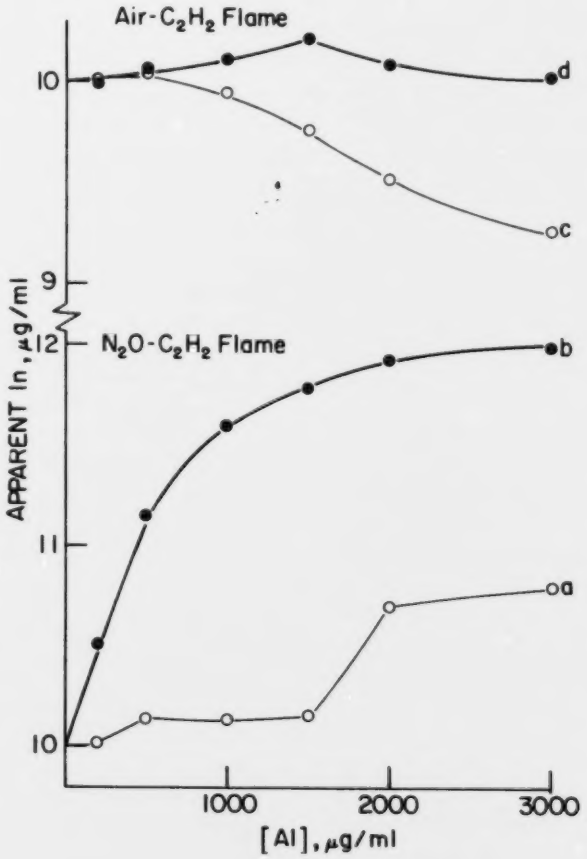

Fig. 5 - Effect of aluminum on the determination of indium by AAS in hydrochloric acid media

a and c - 2000 µg K/mL present in the test and calibration solutions

b and d - K absent in the test and calibration solutions

All solutions contained 10% by volume of hydrochloric acid. Five-fold scale expansion used.

five or six measurements. However, they have been included for comparison purposes to show the differences in the magnitudes of the errors obtained in the presence of aluminum and in the absence and presence of potassium under different flame conditions.

ELIMINATION OF INTERFERENCE FROM ALUMINUM IN THE DETERMINATION OF INDIUM BY FAES

Because ores and concentrates often contain an appreciable amount of aluminum, a simple method was required for eliminating or minimizing its interference, particularly in the more sensitive FAES determination of indium in a nitrous oxide-acetylene flame, after its separation by coprecipitation with iron (III). As recommended by Bernal et al. (26), the use of lanthanum (as chloride) for eliminating interference from aluminum and other elements in hydrochloric acid media was investigated. However, although tests showed that, at the 5-µg/mL indium level in the absence of potassium, 5000 µg of lanthanum per mL eliminates interference in the FAES determination from up to 3000 µg of aluminum per mL, high results were still obtained at indium levels below ~2 µg/mL even in the presence of 1000 µg of aluminum per mL. Furthermore, the use of lanthanum is not feasible for FAES work because of the high background emission. The use of magnesium (as chloride) in hydrochloric acid media (17) was also investigated but was found to be ineffective for FAES work. Similarly lanthanum (as nitrate) in nitric acid media was also not effective. In this medium, the addition of lanthanum, in the presence of both potassium and aluminum, resulted in severe depression of indium emission in the nitrous-oxide-acetylene flame. Although some additional tests showed that, in AAS work in hydrochloric acid media, from 2000-5000 µg of lanthanum per mL and from 2000-4000 µg of magnesium per mL will eliminate interference from 3000 µg of aluminum per mL in solutions containing 5 µg of indium per mL, complete elimination of the interference was not obtained at low levels of indium ($\leq$2 µg/mL). Even 1000 µg of aluminum per mL causes high results under these conditions.

Figure 2 (curve a) shows that, in the presence of 2000 µg of potassium per mL, the ef-

fect of aluminum on the determination of indium by FAES in nitric acid media is reasonably constant at concentrations from ~1000-1500 µg/mL. Figure 3(a) (curve a) shows that, at the 2-µg/mL indium level, the same effect occurs when indium is determined by AAS in an air-acetylene flame. This suggested the possibility that the interference of aluminum, particularly for an FAES finish, might be largely minimized by adding ~1000 µg of aluminum per mL as a spectroscopic buffer to both the sample and calibration solutions so that the variations in the aluminum content of different samples would not significantly affect the determination of indium (21). Table 2 shows that, under these conditions, and when the sample and calibration solutions contain ~1500 µg of iron (III) per mL and 5% by volume of nitric acid, the error in the indium result by FAES will be ~+5% at the 1.5-µg/mL level when the sample taken for analysis contains ~25-50 mg of aluminum. At this level, it was also found that the iron (III) concentration of the final sample solution can vary from ~500 to 2000 µg/mL without producing more than ±2.5 to 3% error in the result. As shown later, this is only about twice the magnitude of the precision of the FAES determination. This permissible range of iron concentration is advantageous when the iron content of the sample is not accurately known.

EFFECT OF OTHER ELEMENTS ON THE DETERMINATION OF INDIUM BY FAES AFTER SEPARATION BY IRON COLLECTION

Table 2 shows that, in the presence of aluminum, milligram-quantities of titanium and vanadium enhance indium emission in the nitrous oxide-acetylene flame. The same effects occur in the absence of aluminum. However, relatively large amounts of manganese (II), bismuth, lead, calcium, magnesium, nickel (II), copper (II), cobalt, zinc, molybdenum (VI) and tungsten (VI) can be present during the coprecipitation step without causing appreciable error in the result. The effects of titanium and vanadium were not studied in further detail because they are not usually present in significant amounts in zinc ores, concentrates and processing products. However, they probably react similarly to aluminum because they form more stable oxides than aluminum (27). The effects of tin, arsenic and antimony, which would also be coprecipitated with iron (III), were not investigated because they can readily be removed by volatilization as the bromides during the sample decomposition step.

APPLICATION OF THE IRON COLLECTION AND EXTRACTION METHODS TO CCRMP REFERENCE MATERIALS AND ZINC PROCESSING PRODUCTS

Table 3 shows the results obtained by FAES when the iron collection and extraction methods described in the experimental section above were applied to CCRMP certified reference materials and to actual zinc processing products. Table 4 shows the FAES results obtained for CCRMP materials to which a known amount of indium was added. In this work, the extraction method used at CANMET (1) was modified by increasing the organic:aqueous phase ratio during the extraction step from 0.4:1 to 1:1 to ensure the complete extraction of up to at least 500 µg of indium. The final FAES determination was carried out in a 2% nitric acid medium containing 2000 µg of potassium per mL, rather than the dilute hydrochloric acid medium recommended, and 3 g of ascorbic acid was added before the extraction step to ensure the reduction of all the iron (III) present. Table 3 shows that the results obtained for the CCRMP ores and concentrates by the extraction method are in excellent agreement with each other and in good agreement with, or within the 95% confidence limits of, the certified values or those given for information purposes. From the results obtained in this work (0.066%) and some previous work at CANMET by the extraction method (0.064%), it is considered probable that the certified value for MP-1 is slightly high. The results obtained for the CCRMP materials to which indium was added (Table 4) are also in good agreement with the total calculated amount of indium present. However, both tables show that, in general, the iron collection - FAES method, which involves the use of aluminum as a spectroscopic buffer, is prone to positive error probably because of the cumulative effects of the coprecipitated and occluded elements and, in cases in which the sample also contains aluminum, because of the increased aluminum content of the

Table 2 - Effect of diverse ions on the FAES determination of indium in nitric acid media

Diverse ion taken, mg/100 mL	In taken, µg/100 mL	In found, µg* Without iron collection	In found, µg* With iron collection
Al 25†	150	-	156
50†	150	-	157
100†	150	-	177
Mn(II) 50	40	40.6	-
50	250	254	-
Ti(IV) 1	40	41.5	-
1	250	256	-
3	40	43.8	-
3	250	254	-
5	250	255	-
10	40	61.1	-
10	250	266	-
V(V) 5	150	-	154
10	150	-	166
50	150	-	196
Ti(IV) (1 mg) + V(V) (1 mg)	150	-	157
Ti(IV) (2 mg) + V(V) (2 mg)	150	-	165
Bi 50	40	42.0	-
50	250	249	-
Pb 600	40	40.9	-
600	250	249	-
Pb 500	40	-	39.7
500	250	-	248
W(VI) 50	150	-	153
Zn 500	150	-	150
Mo(VI) 50	150	-	151
Cr(III) 10	150	-	151
Ca (100 mg) + Mg (100 mg) + Ni(II) (100 mg) + Cu(II) (100 mg) + Mn(II) (100 mg) + Co (50 mg)	150	-	149

*Test and calibration solutions contained 1500 µg of iron (III) per mL, 1000 µg of aluminum per mL, 2000 µg of potassium per mL and 5% by volume of nitric acid.

†Extra aluminum added to the test solutions before the iron collection step.

Table 3 - Results obtained by FAES for CCRMP ores and concentrates and for zinc processing products by the iron collection and extraction methods

Sample and mass taken	Nominal composition, %	CCRMP certified value, In, µg/g	In found by FAES, µg/g	
			Iron collection method	Extraction method
CZN-1 Zinc concentrate	0.3 Al_2O_3, 10.9 Fe, 7.5 Pb, 30.2 S 44.7 Zn, 1.0 SiO_2	86 ± 17*	86.7, 90.5, 90.1	87.0, 86.8, 87.0
CPB-1 Lead concentrate	0.3 Al_2O_3, 8.4 Fe, 64.7 Pb, 17.8 S, 4.4 Zn, 0.7 SiO_2, 0.4 Sb, 0.9 CaO	14 ± 3*	13.9, 12.6	10.7, 11.2, 10.8
MP-1 Zinc-tin-copper-lead ore	3.6 Al, 5.7 Fe, 1.9 Pb, 11.8 S, 15.9 Zn, 19.4 Si, 0.8 As, 3.4 CaO, 2.4 Sn, 2.1 Cu, 0.07 Ti	0.069 ± 0.003%	696, 691, 696	659, 659, 659
MP-1a Zinc-tin-copper-lead ore	6.2 Fe, 4.3 Pb, 12.7 S, 19.0 Zn, 41.8 SiO_2, 1.3 Sn, 1.5 Ca, 1.4 Cu	0.033 ± 0.001%	355, 350, 350	330, 327, 328
No. 1 Roaster bed overflow	~60 Zn, ~10 Fe, ~2 S	-	194, 188	195, 191
No. 1 Roaster hot cyclone	~60 Zn, ~10 Fe, ~2 S	-	189, 179	181,181
Neutral leach residue	21.2 Zn, 32.9 Fe, 1.5 Pb	-	585, 600	569, 578
Lead-silver leach residue	8.9 Zn, 22.0 Fe, 6.8 Pb	-	460, 450	448, 441
Jarosite precipitate	32.2 Fe, 1.3 Pb	-	625, 618	621, 600, 610
Combined calcine to leach	61.1 Zn, 9.8 Fe, 2.0 S	-	168, 162	167, 161, 157

*CCRMP value given for information only (not certified).

Table 4 - Results obtained by FAES for CCRMP ores and concentrates by the iron collection and extraction methods after addition of indium

Sample and mass taken	Nominal composition, %	In present in sample, µg/g*	Total In present, µg, after addition of 50 µg	In found by FAES, µg	
				Iron collection method	Extraction method
KC-1 Zinc-lead-tin-silver ore (1 g)	0.8 Al, 16.1 Fe, 6.9 Pb, 28.1 S 20.1 Zn, 11.1 Si, 0.7 Sn	2.9, 3.1	53.0	55.6	52.0, 52.5
CCU-1 Copper concentrate (0.5 g)	0.2 Al_2O_3, 30.8 Fe, 35.6 S, 3.2 Zn, 2.6 SiO_2, 1.1 MgO 24.7 Cu	34.6, 34.7	67.4	65.8	65.2, 68.0
(1g)	" " "	-	84.7	-	83.3
SU-1a Nickel-copper-cobalt ore (1 g)	5.0 Al, ~20 Fe, ~10 S, ~38 SiO_2, 3.5 Ca, 3.0 Mg, 1.2 Cu, 1.2 Ni	0.6, 0.5	50.6	70.5, 69.6	52.5, 49.7
HV-1 Copper-molybdenum ore (1 g)	6.6 Al, 1.9 Fe, ~35 S, 33.9 Si, 1.4 Ca, 0.5 Cu, 0.16 Ti	0.8, 0.3	50.6	71.4, 76.4	50.2, 49.5

*Indium determined by the extraction method.

final sample solution compared with the calibration solutions. As mentioned above and shown in Table 2, these effects, particularly those caused by aluminum and titanium, will produce a positive error in the result. This is evident from the results shown for MP-1 in Table 3 and for SU-1a and HV-1 in Table 4. It is not known whether the zinc processing products shown in Table 3 contain aluminum or titanium.

COMPARISON OF FAES AND AAS RESULTS FOR INDIUM

Because interference effects are usually less in AAS than in FAES, some of the sample solutions remaining after the analysis of the CCRMP materials and zinc processing products by FAES were also analyzed by AAS in an air-acetylene flame using the same calibration solutions for comparison purposes. Tenfold scale expansion was used because of the low sensitivity for indium by AAS. Table 5 shows that the results obtained by AAS for the extraction method, in which indium is separated from the matrix elements, are in excellent agreement with those obtained by FAES. However, although the results obtained for the CCRMP materials after the separation of indium by iron collection are all lower than the corresponding FAES results, they are, except for CZN-1 and MP-1, still higher than the recommended values or calculated amounts present and higher than the mean values obtained by the extraction method (Tables 3 and 4). As indicated in Fig. 3(a) (curve a), this positive error is largely caused by the presence of moderate amounts of aluminum in the sample because the apparent indium content increases when the total aluminum content of the sample solution is greater than 1000 µg/mL. The results obtained for SU-1a and HV-1 by both FAES and AAS after separation of indium by iron collection also suggest that the interference of aluminum with both finishes is greater at low levels of indium.

CONCLUSIONS

The results obtained in this investigation show that the best method for the exact, nonroutine determination of indium in ores, concen-

Table 5 - Comparison of FAES and AAS results for indium

	In found, µg/g			
	Iron collection method		Extraction method	
Sample	FAES	AAS	FAES	AAS
CZN-1	90.1	85.9	86.8	87.7
CPB-1	-	-	11.2	11.9
MP-1	696	665	659	652
MP-1a	350	340	327	328
KC-1 + 50 µg In	-	-	52.5	50.0
CCU-1 + 50 µg In	-	-	65.2	65.6
SU-1a + 50 µg In	69.6	63.9	49.7	50.0
HV-1 + 50 µg In	76.4	62.0	49.5	48.8
No. 1 Roaster bed overflow	188	192	191	193
No. 1 Roaster hot cyclone	179	182	181	178
Neutral leach residue	600	600	578	587
Combined calcine to leach	162	157	161	161
DA-6697 In-bearing sodium jarosite	-	-	1035	1040
DA-6698 In-bearing sodium jarosite	-	-	1057	1065
DA-6699 In-bearing sodium jarosite	-	-	1052	1046
DA-6807 Jarosite residue	-	-	1038	1040

trates and zinc processing products is that based on the separation of indium from the matrix elements by extraction as the bromide. Table 6 shows that, by this method, the precision of the results for indium at about the 90-μg/g level or less is better if it is determined by FAES rather than AAS. At about the 1000-μg/g level, the precision for FAES and AAS is about the same. Because of its low sensitivity, AAS is not recommended for the determination of less than ~1 μg/mL of indium. Under the conditions recommended for the extraction of indium, gold (III) and thallium (III) are completely extracted as bromides, tin (II) and tin (IV) are largely extracted, gallium, molybdenum (VI), antimony (III), arsenic (III), selenium (IV) and tellurium (IV) are partly extracted and copper (II) is slightly extracted (28). However, up to ~250 mg of copper can be present in the sample taken for analysis without causing appreciable error in the result and, as mentioned above, tin, arsenic and antimony can readily be removed by volatilization as the bromides during the sample decomposition step. Selenium is also removed by this procedure. Except for molybdenum, the remaining elements would not be expected to be present in sufficient amounts in ores and zinc processing products - relative to indium - to cause significant error in the final FAES or AAS result. The extraction-FAES method is suitable for indium in ores and related materials at levels as low as ~1 μg/g.

The precision of the FAES results shown in Table 6 for the CCRMP materials by the extraction method, and that shown in Table 3 for the same and other CCRMP materials by both the iron collection and extraction methods, is relatively good. However, the precision of the results shown in Table 3 for the zinc processing products is, in most cases, not as good as that obtained (Table 6) for the jarosite residue. To some extent, this could be caused by inhomogeneity because, even though the samples were ground and thoroughly mixed at the beginning of the investigation, some samples clumped into globules in the bottle on standing. To obtain the results shown in Table 3, subsamples of these materials (without further mixing) were taken over a time interval of about one month. For the precision test shown in Table 6, subsamples of the well mixed jarosite residue were taken within two days.

The iron collection method described in this work in conjunction with either a FAES finish in a nitrous oxide-acetylene flame or an AAS finish in an air-acetylene flame can be used for the

Table 6 - Precision for indium by FAES and AAS after separation by extraction

	In found, μg/g				
	CPB-1	CZN-1		Jarosite residue DA-6806	
	FAES	FAES	AAS	FAES	AAS
	11.2	86.8	87.7	1059	1059
	10.8	87.0	85.1	1059	1045
	10.7	87.0	86.2	1030	1037
	11.2	85.8	88.6	1033	1045
	11.4	86.5	89.0	1040	1064
Mean	11.1	86.6	87.3	1044	1050
Standard deviation	0.30	0.50	1.64	13.99	11.14
Relative standard deviation, %	2.7	0.6	1.9	1.3	1.1

determination of ~100μg/g or more of indium in ores and related materials when high accuracy is not required and if the sample does not contain more than ~10 mg of aluminum. For the FAES finish, the titanium or vanadium content of the sample should not exceed ~1 mg. For the AAS finish, up to ~10 mg of either element can be present.

REFERENCES

1. Donaldson, E.M. "Methods for the analysis of ores, rocks and related materials (Second edition)"; Mines Branch Monograph 881; CANMET, Energy, Mines and Resources Canada; 47-49; 1982.

2. Brandenburger, H. and Bader, H. "Flame emission photometry of ether solutions. Detection of gallium, indium and thallium in trace analysis"; Helv Chim Acta 47:353-358; 1964.

3. Hubert, A.E. and Lakin, H.W. "Atomic absorption determination of thallium and indium in geologic materials"; Geochem Explor Proc 4th Int Geochem Explor Symp; 1972, Denver; 383-387; 1973; Chem Abstr 81; 9369g; 1974.

4. Gomez Coedo, A., Dorado Lopez, M.T. and Sistiaga, J.M. "Application of atomic-absorption and plasma spectrometry (ICP) techniques to the determination of indium and thallium in zinc and its alloys"; Rev Metal (Madrid) 15:379-385; 1979; Chem Abstr 93: 60418x; 1980.

5. Popova, S. and Minchev, L. "Atomic-absorption determination of indium in mineral raw materials and industrial wastes"; Rudodobiv 35:25-27; Chem Abstr 93:87884h; 1980.

6. Britske, M.E., Tarasevich, N.I. and Savel'eva, A.N. "Determination of indium by flame photometry"; Sb Nauch Tr Gos Nauch-Issled Inst Tsvet Metal 27:108-116; 1967; Chem Abstr 70:25415x; 1969.

7. Spitzer, H. and Tesik, G. "Determination of indium in plant leach solutions of chloridizing roasting by means of atomic-absorption spectrometry"; Erzmetall 22:383-384; 1969; Chem Abstr 72:62467c; 1970.

8. Jones, A.E. and Lee, A.F. "The determination of thallium and indium in sulphide concentrates"; Nat'l Inst Metall (S. Africa) 2022; 1979.

9. Pilipenko, A.T. and Samchuk, A.I. "Extraction - atomic-absorption determination of indium in minerals"; Zh Anal Khim 34:2128-2133; 1979.

10. Aihara, M. and Kiboku, M. "Extraction and atomic absorption spectrophotometric determination of indium and tellurium by using potassium xanthates"; Bunseki Kagaku 30:295-299; 1981; Chem Abstr 95:54153g; 1981.

11. Aller, A.J. "Solvent extraction - flame spectrometric methods for the determination of indium in aluminum alloys"; Anal Chim Acta 134:293-300; 1982 (and references therein).

12. Talapova, O.M. and Levin, I.S. "Extraction of indium with bis (2-ethylhexyl) hydrogen phosphate and bis (2-ethylhexyl) hydrogen dithiophosphate and its atomic-absorption determination"; Isz Sib Otd Akad Nauk SSR Ser Khim Nauk 2:60-64; 1981; Chem Abstr 95: 34784k; 1981.

13. Clark, J.R. and Viets, J.G. "Multielement extraction system for the determination of 18 trace elements in geochemical samples"; Anal Chem 53:61-70; 1981.

14. Suschenko, V.G., Kopylova, L.A. and Fedyanina, A.V. "Determination of indium in iron slimes and cakes"; Sb Nauch Tr Vses Nauch-Issled Gornomet Inst Tsvet Metal 13:78-79; 1968; Chem Abstr 72:8937t; 1970.

15. Pickett, E.E. and Koirtyohann, S.R. "The nitrous oxide-acetylene flame in emission analysis - III. Aluminum, gallium, indium, thallium, germanium and tin"; Spectrochim Acta Part B 24:325-333; 1969.

16. Popham, R.E. and Schrenk, W.G. "Atomic absorption characteristics of gallium and indium"; ibid 24:223-233; 1969.

17. Nakahara, T. and Musha, S. "The atomic absorption spectrometric determination of indium in premixed inert gas (entrained air) - hydrogen flames"; Anal Chim Acta 80:47-59; 1975.

18. Haraguchi, H. and Fuwa, K. "Application of molecular-flame-absorption spectroscopy to the elucidation of chemical interferences in indium atomic absorption spectrometry"; Bull Chem Soc Jpn 48:3056-3059; 1975.

19. Fujiwara, K., Haraguchi, H. and Fuwa, K. "Response surface and atomization mechanism in air-acetylene flames. Acid interferences in atomic absorptions of copper and indium"; Anal Chem 47:1670-1673; 1975.

20. Gilbert, P.T. Jr. "Determination of indium by flame photometry"; Spectrochim Acta 12: 397-400; 1958.

21. L'Vov, B.V. "Atomic absorption spectrochemical analysis"; New York, Elsevier; 183-189; 1970.

22. Meloche, V.W., Ramsay, J.B., Mack, D.J. and Philip, T.V. "Determination of indium in aluminum bronze alloys by flame photometry"; Anal Chem 26:1387-1388; 1954.

23. Mulford, C.E. "Gallium and indium determinations by atomic absorption"; Atomic Absorption Newsletter 5:28-30; 1966.

24. Price, W.J. "Spectrochemical analysis by atomic absorption"; London, Heydon; 130-134; 1979.

25. Haraguchi, H., Shiraishi, M. and Fuwa, K. "Recombination reaction between indium and chlorine in air-acetylene flame observed by molecular flame absorption spectroscopy"; Chem Lett 3:251-254; 1973; Chem Abstr 78: 131667f; 1973.

26. Bernal, J.L., Del Nozal, Ma.J., Deban, L. and Aller, A.J. "Determination of indium in aluminum alloys by flame atomic-absorption spectroscopy and flame atomic-emission spectrometry"; Talanta 29:1113-1116; 1982.

27. Reference 21, p 131.

28. De, A.K., Khopkar, S.M. and Chalmers, R.A. "Solvent extraction of metals"; London, Van Nostrand Reinhold; 215-219; 1970.

OPINION POLL

The opinion of concerned readers may influence the direction of future CANMET research.

We invite your assessment of this report - No._____

Is it useful?	Yes_____	No_____
Is it pertinent to an industry problem?	Yes_____	No_____
Is the subject of high priority?	Yes_____	No_____

Comments_____

_____

_____

Please mail to: CANMET Editor, EMR, 555 Booth Street,
Ottawa, Ontario, K1A 0G1

A complimentary copy of the CANMET REVIEW describing CANMET research activity will be sent on request.

CANMET REPORTS

Recent CANMET reports presently available or soon to be released through Printing and Publishing, Supply and Services, Canada (addresses on inside front cover), or from CANMET Publications Office, 555 Booth Street, Ottawa, Ontario, K1A 0G1:

Les récents rapports de CANMET, qui sont présentement disponibles ou qui le seront bientôt peuvent être obtenus de la direction de l'Imprimerie et de l'Edition, Approvisionnements et Services Canada (adresses au verso de la page couverture), ou du Bureau de vente et distribution de CANMET, 555, rue Booth, Ottawa, Ontario, K1A 0G1:

81-13E MA-2: A certified gold reference ore; H.F. Steger and W.S. Bowman;
Cat. No. M38-13/81-13E, ISBN 0-660-11149-7; Price: $2.50 Canada, $3.00 other countries.

82-1E Silica fume in concrete - preliminary investigation; G.G. Carette and V.M. Malhotra;
Cat. No. M38-13/82-1E, ISBN 0-660-11181-0; Price: $6.50 Canada, $7.80 other countries.

82-2E Impact of excessive aromatics in oil sand syndrudes on production and quality of middle distillate fuels; M.F. Wilson;
Cat. No. M38-13/82-2E, ISBN 0-660-11157-8; Price: $2.75 Canada, $3.30 other countries.

82-4E The chemistry, generation and treatment of thiosalts in milling effluents - A non-critical summary of CANMET investigations 1976-1982; edited and compiled by M. Wasserlauf and J.E. Dutrizac;
Cat. No. M38-13/82-4E, ISBN 0-660-11276-0; Price: $9.00 Canada, $10.80 other countries.

82-6E BL-2a and BL-4a: Certified uranium reference ores; H.F. Steger, W.S. Bowman and J. Zechanowitsch and R. Sutarno;
Cat. No. M38-13/82-6E, ISBN 0-660-11179-9; Price: $4.95 Canada, $5.95 other countries.

82-7E Small-scale continuous selective flotation of a New Brunswick massive sulphide ore;
A.I. Stemerowicz, T.F. Berry, R.H. Bredin and G.W. Leigh;
Cat. No. M38-13/82-7E, ISBN 0-660-11247-7; Price: $5.50 Canada, $6.60 other countries.

82-8E Canadian R&D studies of partially briquetted coke oven charges; J.T. Price, J.F. Gransden and W.R. Leeder;
Cat. No. M38-13/82-8E, ISBN 0-660-11217-5; Price: $4.50 Canada, $5.40 other countries.

82-9E CANMET Review 1981-82; Staff of Technology Information Divison;
Cat. No. M38-13/82-9E, ISBN 0-660-11310-4; Price: $5.00 Canada, $6.00 other countries.

82-9F Revue de CANMET 1981-82; Staff of Technology Information Divison;
Cat. No. M38-13/82-9F; ISBN 0-660-91054-3; Price: $5.00 Canada, $6.00 other countries.

82-11E Summaries of CANMET energy research contracts; compiled by T.P. Lanzer;
Cat. No. M38-13/82-11E; ISBN 0-660-11327-9; Price: $6.75 Canada, $8.10 other countries.

82-14E MP-1a: A certified reference ore; H.F. Steger and W.S. Bowman;
Cat. No. M38-13/82-14E; ISBN 0-660-11234-5; Price: $2.50 Canada, $3.00 other countries.

83-3E Certified reference materials; compiled by H.F. Steger;
Cat. No. M38-13/83-3E; ISBN 0-660-11338-4; Price: $5.25 Canada, $6.30 other countries.

83-3F Matériaux de référence; compilé par H.F. Steger;
Cat. No. M38-13/83-3F; ISBN 0-660-91047-0; Price: $5.25 Canada, $6.30 other countries.